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and Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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SCIENTIFIC OFFICER:

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6

ATOMIC AND MOLECULAR PROCESSES.

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TECHNICAL PROGRESS REPORT NO. 23

Pittsburgh Atomic Sciences Institute

University of Pittsburgh

Pittsburgh, PA 15260

I. Summary of Research

This semi-annual progress report contains descriptions of the researches carried out under contract N00014-76-C-0098 during the period April 1977 to September 1977, identifying the topics by title, senior investigator(s) in charge of the work, and the general program to which they belong.

A. Laser Physics1. Energy Transfer Processes of Laser Interest (F. Kaufman and E. C. Zipf)a. F. Kaufman's Group

Excellent progress was made in three areas of our studies of V-V and V-E processes using our fast-flow infrared chemiluminescence apparatus.

(a) The quantitative characterization of $V \rightarrow E$ processes in the $\text{HCl}^V + \text{ICl} \rightarrow \text{HCl}^{V-n} + \text{ICl}^*$ system showed them to be much slower than our qualitative estimate of the last progress report ($k \leq 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$) had indicated. The experiment was carried out by the simultaneous measurement of HCl^V in $v = 1$ to 7 resulting from the $\text{H} + \text{Cl}_2$, $\text{H} + \text{NOCl}$, and $\text{H} + \text{ICl}$ reactions by IR emission in the fundamental and first overtone region, and of the red to near IR emission of ICl and/or high overtone transitions of HCl^V by photomultiplier detection (RCA 31034A) at 630 to 870 nm. The latter emission was calibrated in the same apparatus by measuring the intensity of the $\text{O} + \text{NO}$ chemiluminescence for known concentrations of $[\text{O}]$ by NO_2 -titration, of $[\text{NO}]$ by flow and pressure measurements, and using the absolute rate constant for the $\text{O} + \text{NO}$ emission previously determined in our laboratory.

If we assume that HCl^v in $v \geq 5$ can take part in the above $V \rightarrow E$ reaction and use the measured $[\text{HCl}^v \geq 5]$ obtained from the IR spectral measurements, we calculate $k_{V \rightarrow E} = 1 \text{ to } 2 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$, about three orders of magnitude smaller than the earlier, qualitative estimate. Moreover, even this value is an upper limit, because the emission at 630 to 870 nm includes contributions from the $\Delta v = 5$ and 6 transitions of HCl^v which lie in that same wavelength range and whose A-values are known. These include the $5 \rightarrow 0$, $6 \rightarrow 1$, and $7 \rightarrow 2$ as well as the $6 \rightarrow 0$ and $7 \rightarrow 1$ transitions. When these contributions are added together it appears that about half the observed intensity is due to overtone emission, i.e. $k_{V \rightarrow E} \lesssim 1 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$. If part of the $4 \rightarrow 0$ transition is detected within our bandpass, even this very small $V \rightarrow E$ probability of $\lesssim 10^{-6}$ per collision may be an overestimate.

(b) A large number of V-V transfer rate constants were measured for HCl^v using the steady-state, pseudo-stirred-flow method and using the $\text{H} + \text{ICl}$ reaction to product HCl^v in $v \leq 7$. Table 1 shows results for 9 quenching molecules which were chosen to show the contributions of frequency resonance, dipole moment, and dispersion effects. Although no quantitative picture emerges, certain trends are clear:

Table 1

Quenching of HCl^v by MRate Constant, k_Q , ($10^{-13} \text{ cm}^3 \text{ sec}^{-1}$)

v	$Q = \text{HCl}^0$	CO_2	CH_4	SF_6	CH_3Cl	CH_3F	CCl_4	CF_4	CF_3Br
1	(0.5)	-	17	0.2	140	460	250	-	30
2	35 ± 11	40 ± 30	25	0.1	110	430	230	1.7	18
3	69 ± 29	190 ± 30	21	0.1	160	300	130	1.7	10
4	64 ± 23	380 ± 60	28	0.2	500	670	100	2.2	13
5	150 ± 50	590 ± 70	57	0.2	1100	1300	110	1.6	23
6	320 ± 40	550 ± 100	103		1600	2100	180	2.2	29
7	490 ± 90	410 ± 250	156		1500	1400	240	2.2	50

Energy resonance is the single most important factor for these quenchers. SF_6 and CF_4 are very slow, presumably because they do not have high frequency vibrations. Dipole moment has a small-to-moderate effect (CH_3Cl vs. CH_3F , CF_3Br vs. CF_4 , and CH_4 vs. CH_3F) and dispersion (Van der Waals, polarizability) effects are also moderately large (CCl_4 vs. CF_4). The present data are somewhat crude and will have to be verified by other methods, but they represent the first such measurements anywhere.

(c) Lastly a series of experiments was performed to shed light on the surface deactivation of HCl^v both as to its speed and to its mechanism, i.e. step-by-step cascade in $\Delta v = 1$ increments versus full deactivation in one encounter. In one approach to this problem, the $\text{H} + \text{Cl}_2$ reaction was used to form HCl^v in $v \leq 4$, large excess Cl_2 was used to drive the reaction to completion, and the $[\text{HCl}^v]$ vs. t behavior was modelled, disregarding cascade effects, by integrating the differential equation under conditions where surface deactivation is the principal loss process. Surprisingly, the total rate constant for removal showed a large increase from $v = 1$ ($\sim 100 \text{ sec}^{-1}$) to $v = 4$ ($\sim 600 \text{ sec}^{-1}$). The effects of both radiative and surface reaction cascade were then introduced into the data analysis. Experiments at very low flow velocity ($\sim 1200 \text{ cm sec}^{-1}$ compared with $\sim 10,000$ at full pumping speed) showed the effective surface rate constant, k_w , to be independent of v and to be about 300 sec^{-1} at 0.6 torr flow tube pressure. The cascade effect was then examined by plotting the effective loss rate constant k_e vs. $[\text{HCl}^{v+1}]/[\text{HCl}^v]$ under conditions where $[\text{HCl}^{v+2}]$ was negligible. From these slopes it appears that the deactivation is indeed stepwise, i.e. $\Delta v = 1$, rather than complete in one surface relaxation event. This was further confirmed at pressures from about 0.3 to 7 torr. Further work is in progress to verify this important result and to extend the measurements to other vibrationally excited species.

b. E. C. Zipf's Group

Our Time-of-Flight (TOF) apparatus is presently being modified so that we can measure the cross sections for electron-impact excitation and ionization of atomic and molecular metastable targets. Testing is underway on a new type of high-resolution electron energy analyzer that will be part of this apparatus and provisions are being made for Rydberg atom-ion angular distribution studies. Our TOF work on H_2 , D_2 and HD has now been published. These experiments revealed some new complexities not explained by the core-ion model of dissociation and parallel studies on the excited H atoms created when methane and other light hydrocarbons are dissociated by electron-impact produced evidence showing the $H(3p)$ sublevel is populated by this process contrary to the findings of the Amsterdam group.

2. Electron-Ion Recombination under Laser Plasma Conditions (M. A. Biondi)

The electron-ion recombination studies for molecular noble gas ions of interest to noble-gas halide excimer (e.g. KrF, XeF) laser modelling have continued. The results for krypton will appear in an article in the November issue of Physical Review A. The results are,

$$\alpha(Kr_2^+) = 1.6 \times 10^{-6} [300/T_e(K)]^{0.55} \text{ cm}^3/\text{sec} ,$$

accurate to $\pm 10\%$ over the range $300 \text{ K} \leq T_e \leq 8000 \text{ K}$, with $T_+ = T_{\text{gas}} = 300 \text{ K}$. The excited states of krypton formed by this dissociative recombination process have been determined. The $5p$ and $5p'$ (modified Racah notation) states are most strongly populated over the whole range of T_e .

The studies of argon are nearing completion and will be submitted for publication shortly. The results are,

$$\alpha(Ar_2^+) = 9.1 \times 10^{-7} [300/T_e(K)]^{0.61} \text{ cm}^3/\text{sec} ,$$

accurate to $\pm 10\%$ over the range $300 \text{ K} \leq T_e \leq 8500 \text{ K}$, with $T_+ = T_{\text{gas}} = 300 \text{ K}$. Many different excited states are formed in the recombination process, with the $4p$ and $4p'$ states, lying $\sim 0.9 - 1.4 \text{ eV}$ below the Ar_2^+ ground electronic and vibrational state, the most heavily populated over the quoted T_e range.

3. Ion-Molecule Charge Transfer Processes (M. A. Biondi)

In view of the interest in neon as well as argon as the main fill gas of noble-gas halide excimer lasers, we have used the drift tube/mass spectrometer apparatus to determine reaction rates or set upper bounds on the following charge and atom transfer reactions:

<u>reaction</u>	<u>$k(\text{cm}^3/\text{sec})$</u>	<u>energy range (eV)</u>
$\text{Ar}^+ + \text{Kr} \rightarrow \text{Ar} + \text{Kr}^+$	$< 10^{-14}$	0.04 - 0.1
$\text{Ar}_2^+ + \text{Kr} \rightarrow 2 \text{Ar} + \text{Kr}^+$	$(6 \pm 2) \times 10^{-10}$	0.04 - 1.5
$\text{Ne}^+ + \text{Kr} \rightarrow \text{Ne} + \text{Kr}^+$	$< 10^{-14}$	0.04 - 0.1
$\text{Ne}_2^+ + \text{Kr} \begin{cases} \rightarrow 2 \text{Ne} + \text{Kr}^+ \\ \rightarrow \text{Ne} + \text{Ne Kr}^+ \end{cases}$	$< 10^{-13}$	0.04 - 0.1
$\text{Ne}^+ + \text{Xe} \rightarrow \text{Ne} + \text{Xe}^+$	$< 10^{-14}$	0.04 - 0.1
$\text{Ne}_2^+ + \text{Xe} \begin{cases} \rightarrow 2 \text{Ne} + \text{Xe}^+ \\ \rightarrow \text{Ne} + \text{Ne Xe}^+ \end{cases}$	$< 10^{-13}$	0.04 - 0.1

Thus, although the $\text{Ar}_2^+ + \text{Kr}$ reaction is fast, all others, including $\text{Ne}_2^+ + \text{Kr}$ and Xe are very slow.

4. Dissociative Excitation of Molecules by Electron Impact (E. C. Zipf)

We have completed our studies on electron impact dissociation and excitation of N_2 . This work has led to the measurement of several hundred excitation cross sections from threshold to about 400 eV and has resulted in the identification of the principal channels through which N_2 dissociates. A forbidden predissociation process involving the manifold of discrete $1\pi_u$ and $1\Sigma_u^+$ states is by far the most important mechanism. These studies have

resulted in a detailed quantitative understanding of the N_2 dissociation cross section of Winters and of the role of extreme ultraviolet radiation in the dissociation of N_2 . Using these results it is possible to construct realistic models of the rate of N_2 dissociation under a variety of discharge and shock wave conditions and it is possible to show that N_2 can be dissociated quite efficiently if you proceed in the right manner.

Similar studies on the dissociative excitation of O_2 have shown that there are major errors in the NBS transition probability tabulation for atomic oxygen. The problem is most acute for the $nd\ 3D^o$ and $ns\ 3S^o$ manifolds where the transition probabilities for the intercombination or cascade transitions appear to be in error by a factor of 500 or more. These studies along with tropical airglow measurements also show that current quantum mechanical calculations of $O^+ + e$ radiative recombination also contains order of magnitude errors. There are also significant differences between calculated cross sections for electron-impact excitation of atomic oxygen and measured values. The reason for the failure of conventional theoretical models for these processes in O is not clear, nor can we tell at this point to what extent such errors are present in the tabulated results for other atoms.

5. Theoretical Calculations of Ion-Ion Recombination, V-E Transfer Reactions

Excimer Curves and Electron Excitation of Atoms and Molecules (J. N. Bardsley)

A. Photon and electron collisions with excited rare gas atoms

In collaboration with D. Robb we have begun to explore the application of R-matrix techniques to study the properties of metastable states. Initial studies on He have given promising results for photoionization but have revealed that some changes have to be made in the manner in which the computer code is used.

B. Three-body recombination of ions

Classical calculations were completed of the rates of recombination for several systems of interest in relation to rare-gas halide and mercury-halide lasers, based on the method of Natanson. It was then realized that this theory contains some inconsistent assumptions. This inconsistency has been removed and the new results were accepted for publication. The classical approach is clearly insufficient either to give a definitive value for the recombination rate, or to give information concerning branching ratios. A study of alternative, Monte Carlo, calculations is thus being initiated.

C. Optics

1. Particulate Technology (W. L. Fite)

During the present reporting period activities have been two.

First using a Berglund-Liu monodisperse aerosol generator, measurements have been made of the pulse height distribution for surface ionization detection of particulates of the same size and chemical composition (NaCl, KCl and CsCl). The experiments required making a circuit to transform the slow pulses from the surface ionization process into fast pulses that could be handled by a conventional pulse height generator. The experiments were carried out with hot surfaces placed in a flow tube which fairly reasonably duplicates the stratospheric pressures and parachute drop speeds.

The pulse height distributions for particles with diameters larger than one micron were found to be very broad, making it doubtful that the hot wire detector in stratospheric experiments will yield good information on particle size distribution. However, variations in pulse height distributions with geometry of the active elements in the detector have been noted and we are in the process of trying to find an optimum geometry to narrow the pulse height distributions.

These later experiments are somewhat in contradiction to earlier experiments where narrower pulse height distributions had been observed; we do not understand the difference in results.

The second activity has been preparation of surfaces for surface ionization detection of particulates which do not contain surface ionizable constituents, and particularly will be able to detect ice crystals. The goal is to be able to build a dual surface ionization detector which will be able to distinguish meteoric dusts from ice crystals in the upper atmosphere. The experiment is progressing satisfactorily.

II. Publications and Technical Presentations

A. Publications

Calculations of ion-ion recombination at high pressures, J. M. Wadehra and J. N. Bardsley, Applied Physics Letters, 1978 (in press).

Velocity and energy relaxation of ions in drift tubes, S. L. Lin, L. A. Viehland, E. A. Mason, J. H. Whealton and J. N. Bardsley, J. Phys. B, 1977 (in press).

Dissociative recombination in krypton: dependence of the total rate coefficient and excited-state production on electron temperature, Yueh-Jaw Shiu and Manfred A. Biondi, Phys. Rev. A (Nov. 1977).

Fluorescence lifetime studies of NO₂: I. Excitation of the perturbed ²B₂ state near 600 nm, V. M. Donnelly and F. Kaufman, J. Chem. Phys. 66, 4100 (1977).

Characteristics of OI and NI resonance line broadening in low pressure helium discharge lamps, W. T. Rawlins and F. Kaufman, J. Quant. Spectrosc. and Radiat. Trans., in press.

Mechanism of NO₂ fluorescence quenching, V. M. Donnelly and F. Kaufman J. Chem. Phys., in press.

Dissociative excitation of H₂, HD, and D₂ by electron impact, B. L. Carnahan and E. C. Zipf, Phys. Rev. A, 16, 991, 1977.

On the excitation of Lyman β and Balmer α radiation by electron impact dissociation of methane, R. W. McLaughlin and E. C. Zipf, submitted to Chem. Phys. Lett.

On the dissociation of nitrogen by electron impact and EUV photoabsorption, E. C. Zipf and R. W. McLaughlin, accepted by Planet. Space Sci.

A study of the excitation and radiative decay of the $3s' \ ^3P^o$ and $3d \ ^3P^o$ levels of atomic oxygen, R. W. McLaughlin, E. C. Zipf, and M. R. Gorman, submitted to Planet. Space Sci.

B. Technical Presentations

Kinetics of ClO_x Reactions and the Fluorocarbon-Ozone Problem, F. Kaufman, Colloquium, National Bureau of Standards, 22 April 1977.

Elementary Gas Reactions in Flow Reactors for Science and Society, F. Kaufman 6th Annual G. B. Kistiakowsky Lecture at Harvard University, 4 May 1977.

A series of Five Lectures on Kinetics of Stratospheric Reactions, NO_2 Fluorescence, Hydrogen Atom Recombination, Apollo-Soyuz Ultraviolet Absorption Experiment, and Vibrational Relaxation, F. Kaufman, Institut für Physikalische Chemie der Universität Göttingen, May and June 1977.

Kinetics of Neutral-Neutral Reactions: An overview, F. Kaufman, Plenary Lecture at 3rd International Symposium of Plasma Chemistry, IUPAC, Limoges, France, 15 July 1977.

Chlorine Reactions, F. Kaufman, Invited lecture at IAGA Symposium Honoring Marcel Nicolet, University of Washington, 22 August 1977.

Elementary Gas Reactions in Flow Reactors: Experiment, Theory and Application, F. Kaufman, Colloquium, Carnegie-Mellon University, 8 September 1977.

C. Other Activities Relating to ARPA

J. N. Bardsley and M. A. Biondi attended the ARPA review of Avco Everett's Visible Laser Program, Boston, May 25-27, 1977.

J. N. Bardsley and M. A. Biondi attended the ARPA Institutes & University Program Review meeting in Washington, D. C., May 4-6, 1977.

F. Kaufman attended the Office Advisory Board meeting of the Office of Chemistry and Chemical Technology, National Academy of Sciences, at Washington, D. C., 23 April 1977.

F. Kaufman attended the semi-annual meeting of the AFOSR Chemistry Panel at Bolling Air Force Base on 12 and 13 May 1977.

III. Visiting Scientists

A. Lifshitz, Hebrew University
G. Skinner, Wright State University
S. L. Lin, Brown University

IV. Degrees Awarded

J. S. Chang, Ph.D., September 1977

Senior InvestigatorEstimated Funds Expended and Committed (Thousands)

J. N. Bardsley	\$ 41.0
M. A. Biondi	117.0
W. L. Fite	40.0
F. Kaufman	91.0
E. C. Zipf	<u>30.5</u>
Total Expended and Committed	319.5
Available Funds	<u>335.0</u>
Estimated Funds Remaining as of 9/30/77	15.5

University Accounting of Funds

Expended as of 9/30/77	318.9
Available Funds	<u>335.0</u>
Remaining Funds as of 9/30/77	16.1